Pilot Studies of a Novel Ozonation/Fluidized Bed Treatment Process for Disinfection By-product Control

Project Scope

Natural organic matter (NOM) is a complex mixture of organic materials normally present in source waters. During drinking water treatment, chlorine comes in contact with NOM which causes the formation of trihalomethanes (THMs) and other halogenated compounds. The formation of THMs and other disinfection byproducts (DBPs) during the disinfection of drinking waters may pose a public health risk as a number of DBPs, including chloroform and dichloroacetic acid, have been shown to be either carcinogenic or potentially carcinogenic. A number of DBPs, including dichloroacetic acid, have also been shown to have substantial toxicity.

Many drinking water utilities worldwide are currently using ozonation followed by biological filtration (biodegradation of organic matter by microorganisms) to remove organic matter and to control DBP precursors in drinking water. Although diverse in nature, NOM can be divided into the following three classes: (1) rapidly biodegradable organic matter (biodegrades within minutes of contact with biofilters); (2) slowly biodegradable organic matter (requires hours of contact time for biodegradation); and (3) non-biodegradable organic matter (does not biodegrade after two hours of contact time). Ozonation converts non-biodegradable organic matter into biodegradable organic carbon (BDOC). BDOC that remains in drinking water after treatment can cause DBP formation and can support the growth of microorganisms, including pathogenic bacteria, in the distribution system. The amount of organic matter is often expressed in terms of the total organic carbon (TOC) or dissolved organic carbon (DOC), both of which include BDOC.

This research grant investigated a combined ozonation/biological fluidized bed treatment (FBT) for the removal of DBP precursors from drinking water. FBT differs from standard biofiltration. In a standard biofilter, water flows downward by the force of gravity, which tends to pack the colonizing microorganisms. In an FBT column, water flows upward which suspends the support medium, increasing

Grant Title and Principal Investigator

Pilot Studies of the Ozonation/FBT Process for the Control of Disinfection Byproducts in Drinking Water (EPA Grant #R826829)

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Key Findings and Implications

Analytical Accomplishments:

- Three different surface waters were tested and found to have differing natural organic matter (NOM) that responds to biodegradation in different ways. Ozonation also had differing effects on the NOM present in the different waters.
- A bench-scale fluidized bed treatment (FBT) was found to remove fast biodegradable organic carbon (BDOC) in less than 30 minutes, while biofiltration required 50 minutes to remove fast BDOC.
- Addition of an easily biodegradable carbon source can stimulate more rapid biodegradation and can decrease the concentration of $BDOC_{slow}$.
- Peroxone-FBT shows better removal efficiency of total organic carbon and UV absorbance compared to ozone-FBT and is cost competitive compared to ozone-FBT.

Implications of Research and Impacts of Results:

- Cost estimates indicate that ozonation-FBT systems could be cost-effective for small utilities, and for larger utilities with limited space for retrofitting or expansion.

Publications include 3 peer reviewed journal articles and 5 conference presentations.

Project Period: July 1998 to August 2002

Relevance to ORD's *Drinking Water Research Multi-Year Plan* (2003 Edition)

This project contributes directly to two of three Long-term Goals for drinking water research: (1) by 2010, develop scientifically sound data and approaches to assess and manage risks to human health posed by exposure to regulated waterborne pathogens and chemicals, including those addressed by the Arsenic, M/DPB, and Six-Year Review Rules; and (3) by 2009, provide data, tools, and technologies to support management decisions by the Office of Water, state, local authorities, and utilities to protect source water and the quality of water in the distribution system.

An ozonation-fluidized bed treatment (FBT) system was designed and tested using three surface waters sources of drinking water with differing types of natural organic matter. The system can be further optimized by the addition of an easily biodegradable carbon source to act as a biostimulant (increases microbial biodegradation rate). Research was also initiated using a peroxone (combination of ozone and hydrogen peroxide)-FBT system, which may provide better treatment efficacy than the ozonation-FBT system.

the surface area and promoting greater biomass attachment and degradation. The specific objectives of this grant were to:

1. Develop an economical and simple processing system for the control of DBPs in drinking water while maintaining adequate disinfection;
2. Develop design criteria for the proposed ozonation-FBT system; and
3. Investigate the use of FBT systems to accomplish "stimulated" biodegradation of organic matter.

The studies were conducted using three source waters: (1) Lake Erie water collected at the Monroe Water Filtration Plant (Monroe, Michigan; Lake Erie water has a low TOC concentration of approximately 2 mg/L); (2) Huron River water collected at the Ann Arbor Water Treatment Plant (Ann Arbor, Michigan; Huron River water has a TOC concentration of 6 to 8 mg/L and is typical of rivers across the United States); and (3) Lake Lansing water (East Lansing, Michigan). Although Lake Lansing water does not provide source water to any treatment plant, it was selected because of its high TOC concentration (9 to 11 mg/L).

Project Results and Implications

Three experimental systems were developed to test the effects of ozonation on DBP formation: (1) bench-scale ozonation, (2) bench-scale FBT biodegradation, and (3) pilot-scale ozonation/FBT. The rate of biodegradation is faster with an FBT column compared to a standard biofilter. A comparison of bench-top systems with raw water at room temperature demonstrated that FBT was able to remove fast BDOC in less than 30 minutes, whereas biofiltration required 50 minutes to remove fast BDOC. In addition, a treatment cost estimate based on "typical" operating facilities indicated that the ozonation-FBT process may be a viable alternative to conventional processes, especially those that require additional steps such as ozonation and biological activated carbon filtration for the control of DBPs.

<u>Biodegradabity of TOC in Raw Water</u>: The biodegradation kinetics of TOC in raw water from the three sources was characterized in this study. The results demonstrated that the source waters selected for this study were distinctive with regard to the proportion of TOC that was potentially biodegradable (see Figure 1). That is, essentially all of the organic matter in Lake Erie water was resistant to biodegradation. TOC from Huron River water was approximately 20 percent potential BDOC, whereas nearly one-half of the organic matter in Lake Lansing could be biodegraded.

<u>Biodegradation of Ozonated Water</u>: Ozonation of Lake Erie water at doses up to 3 mg O_3/mg C did not result in the production of BDOC. Ozonation of Huron River water resulted in an increase of BDOC

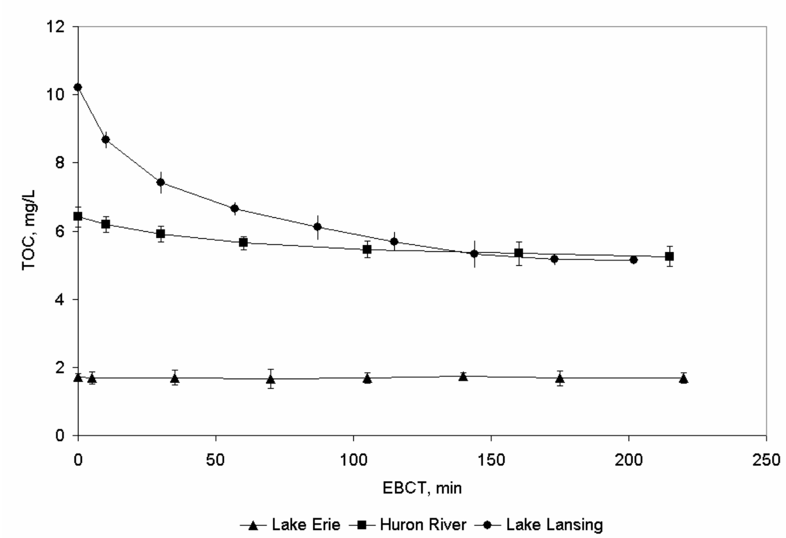

Figure 1. Biodegradation kinetics of raw water.

concentration from 1.2 mg/L in raw water to 2.8 mg/L in water that had been ozonated at a dose of 1 mg O_3/mg C. Because there was little difference between 0.5 mg O_3/mg C and 1 mg O_3/mg C, higher ozonation doses were not tested on Huron River water. In contrast, Lake Lansing water BDOC did increase as increasing ozone doses were applied. Ozonation of Lake Lansing water at a dose of 0.75 O_3/mg C resulted in an increase in BDOC concentration from 5.04 (in raw water) to 6.06 mg/L. Ozonation at ozone doses of 1.5 and 3 mg O_3/mg C resulted in the formation of additional 0.8 and 1.33 mg/L BDOC, respectively. An increase in ozone dose also resulted in an increase in the rate of biodegradation (R_{max}) and a decrease in the minimum empty bed contact time required to biodegrade the rapidly degrading BDOC (fast BDOC) in Lake Lansing water.

In the United States, the control of BDOC produced by ozonation is typically accomplished by rapid filtration with an empty bed contact time of 15 to 20 minutes. Although the results of this research project suggest that these filters are capable of removing fast BDOC from ozonated water, the more slowly degrading BDOC ($BDOC_{slow}$) would remain in the filter effluent. This remaining BDOC may support bacterial growth in the distribution system. Thus, the control of $BDOC_{slow}$ produced or remaining after ozonation may be a critical consideration in the design of water treatment systems employing ozonation. Experiments were conducted to investigate the reactions of NOM during ozonation. How ozone reacts with NOM was found to be affected by the following parameters: NOM chemical characteristics, initial $[O_3]/[NOM]$ concentration ratio, pH, buffering capacity, reaction temperature, reaction time (constant ratio between OH radical and molecular ozone concentration), and additives concentration (biocarbonate and phosphate ion).

Pilot-Scale Studies: Pilot-scale studies were conducted from November 2000 to May 2001 at the ozonation-FBT system at the Monroe Water Treatment Plant in Monroe, Michigan. As expected, because of the limited formation of BDOC after ozonation of Lake Erie water, the ozone/FBT system was not effective in removing organic carbon and DBP precursors (which were low to begin with). This indicates that Lake Erie water TOC level (2 mg/L) is below the threshold for the process's effectiveness. Another pilot-scale plant was installed in Ann Arbor in June of 2001. The ozone dose to Huron River water was maintained at a level of approximately 0.5 mg O_3 /mg C, and the retention time in the FBT column was about 5 minutes. The ozonation-FBT system reduced turbidity to levels that would be acceptable for subsequent direct filtration. However, no appreciable reduction in TOC and DBP precursors was achieved. This was expected, based on the bench-scale testing with the Huron River water, which suggested that at least 30 minutes retention time was needed to achieve 30 to 40 percent TOC removal. The results of the bench-scale and pilot-scale studies indicate that the ozonation-FBT system would be most effective for the treatment of contaminated source waters having a TOC concentration of 4 mg/L and higher if the TOC is BDOC or convertible to BDOC by ozonation.

Biostimulation: Addition of a small amount of an easily biodegradable carbon source (2.5 mg/L of acetate) added to Huron River water acted as a biostimulant which resulted in a nearly two-fold decrease in $EBCT_{min}$ compared to treatment without biostimulation. Biostimulation also decreased the concentration of $BDOC_{slow}$ from 0.79 mg/L min to 0.47 mg/L min.

Peroxone-FBT: Lake Lansing water was used to test a combination of ozone and hydrogen peroxide, known as the peroxone system. Ozonation destroys the aromatic portion of NOM without TOC removal by the direct reaction involving molecular ozone. Peroxone appears to more randomly attack NOM by increasing OH radical concentration. This could account for the enhanced removal efficiencies of TOC and UV absorbance with peroxone compared to ozonation. A cost estimation indicated that peroxone could be competitive with ozonation.

Summary: Differences in ozone reactivity with TOC from different source waters were investigated in this project. The biodegradability of ozonated TOC by FBT was investigated, and the effectiveness of combined ozonation-FBT systems for selected source waters with high TOC levels was demonstrated. Design criteria for the ozonation-FBT systems were developed based on studies of pilot-scale systems. Costs of the combined ozonation-FBT process were found to be competitive with conventional water treatment processes and could be cost-effective for small utilities, and for larger utilities with limited space for retrofitting or expansion.

Investigator

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For More Information

NCER Project Abstract and Reports:

http://cfpub2.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/41/report/0

Peer Reviewed Publications

Yavich, A.A., Lee, K-H., Chen, K-C., Pape, L., and Masten, S.J. 2004. Evaluation of biodegradability of NOM after ozonation. Water Research 38:2839-2846.

Yavich, A.A., and Masten, S.J. 2003. The use of ozonation and FBT to control THM precursors. Journal of the American Water Works Association 95(4):159-171.

Yavich, A.A., and Masten, S.J. 2001. Modeling the kinetics of ozone reactions with NOM in Huron river water. Ozone: Science and Engineering 23(2):105-119.